

Supplementary Material (ESI) for Chemical Communications
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Supporting Information for:

Unusual Mesomorphic Behaviour of an Ethynyl-Substituted Phthalocyanine

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General Methods:

Most of the solvents employed in this work were purchased from SDS. All dry solvents were freshly distilled under argon over an appropriate drying agent before use. Chemicals were purchased from Aldrich Chemical Co., Acros Organics or Fluka Chemie and used as received without further purification. The monitoring of the reactions has been carried out by thin layer chromatography (TLC), employing aluminum sheets precoated with silica gel 60 F₂₅₄ (Merck). The purification and isolation of most of the products was performed by column chromatography using silica gel Merck-60 (230-400 mesh, 0.040-0.063 mm).

Melting points (m.p.) were determined in a Büchi 504392-S equipment and are uncorrected.

¹H nuclear magnetic resonance (NMR) spectra were recorded with a BRUKER AC-200 (200 MHz) or a BRUKER AC-300 (300 MHz) instrument. In all cases the deuterated solvent employed was CDCl₃. Chemical shift values (δ) are referred to tetramethylsilane (TMS), utilized as an internal reference.

MALDI-TOF mass spectrometry (MS) spectra were obtained from an Applied Biosystem 4700 instrument equipped with a Nd:YAG laser operating at 355 nm at the Servicio Interdepartamental de Investigación (SIdI) of the Universidad Autónoma de

Madrid (UAM). The matrix utilized was in all cases dithranol. Relative intensity values for the most relevant ion peaks are indicated in brackets.

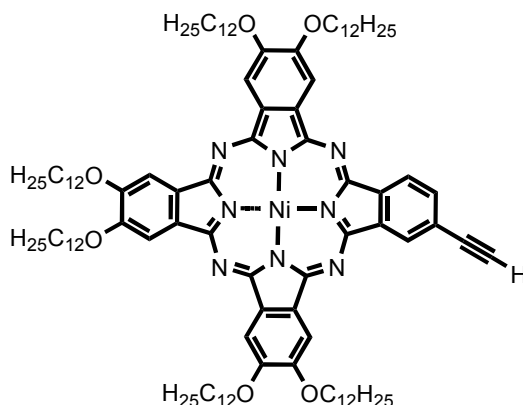
UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. The solvents employed in this technique (usually CHCl_3) were purchased from Fluka Chemie. The logarithm of the absorption coefficient (ϵ) is indicated in brackets for each maximum.

Infrared (IR) spectra were recorded on a Bruker Vector 22 spectrophotometer, in the Departamento de Química Orgánica of the UAM, employing in all cases solid samples (KBr pressed disks).

Elemental analysis were performed in the Servicio Interdepartamental de Investigación (SIdI) of the Universidad Autónoma de Madrid. A Perkin Elmer 2400 CHN or a Perkin Elmer 2400 CHNS/O 2400-II analyzer were employed.

The optical textures of the mesophases were investigated with a Nikon polarizing microscope equipped with a Linkam THMS600 hot stage. The transition temperatures and enthalpies were measured by differential scanning calorimetry (DSC) with a TA Instruments DSC-2910 operated at a scanning rate of $10\text{ }^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. The apparatus was calibrated with indium ($156.6\text{ }^\circ\text{C}$, 28.4 J g^{-1}) as a standard. Thermogravimetric analyses (TGA) were performed using TA Instruments STD-2960 with simultaneous DTA-TGA at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. X-ray diffraction patterns were obtained using a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered $\text{Cu-K}\alpha$ beam. The sample was held in Lindeman glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on flat photographic film.

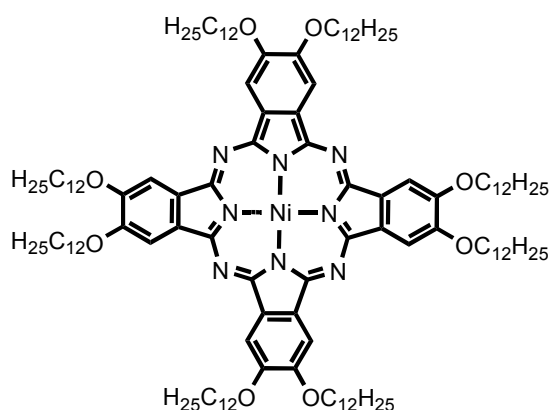
2-Ethynyl-9,10,16,17,23,24-hexakis(dodecyloxy)phthalocyaninatonicel(II) (1)



2-(3-hydroxy-3-methyl-1-butynyl)-9,10,16,17,23,24 hexakis(dodecyloxy) phthalocyaninatonicel(II) (**3**) (71 mg, 0.04 mmol) and finely grounded sodium hydroxide (3.5 mg, 0.087 mmol) were refluxed in dry toluene (3 mL) under argon for 18 hrs. The solution was then reduced to dryness and the product obtained dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (2 x 100 mL). The organic layer was then separated, dried over Mg_2SO_4 and reduced in volume to obtain a blue product that was subjected to column chromatography on silica gel (CHCl_3 /hexane 2:1) to yield Ni(II)Pc **1** as a blue product (47.6 mg, 70%).

$\text{Col}_h \rightarrow I = 70^\circ\text{C}$; ^1H NMR (CDCl_3): δ 8.0-7.3 (m, 9H, CH_{Ar}), 4.5-4.3 (m, 12H, $-\text{OCH}_2-$), 3.5 (s, 1H, $-\text{C}\equiv\text{CH}$), 2.2-1.3 (m, 108H, $-\text{CH}_2-$), 1.2 (m, 12H, $-\text{CH}_2\text{CH}_3$), 1.0 (m, 18H, $-\text{CH}_3$); MALDI-TOF MS (dithranol): m/z 1699-1704 (isotopic pattern) $[\text{M}]^+$; IR (KBr): ν (cm^{-1}) 3450, 2851, 1281, 1097; UV-vis (CHCl_3) λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 290 (4.74), 618 (4.33), 677 (4.86); elemental analysis for $\text{C}_{106}\text{H}_{160}\text{N}_8\text{O}_6\text{Ni}$ (FW = 1699.2): Calcd: C 74.84%, H 9.48%, N 6.59%. Found: C 75.01%, H 9.42%, N 6.43%.

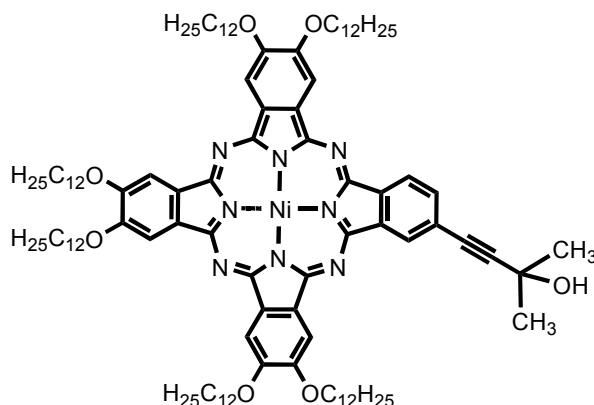
1,2,9,10,16,17,23,24-Octakis(dodecyloxy)phthalocyaninatonickel(II) (2)



The reaction's condition for the synthesis and purification of the Ni(II)Pc **2** are reported in the synthesis of the Ni(II)Pc **1** (*vide infra*).

$K \rightarrow Col_h = 84\text{ }^\circ\text{C}$, $Col_h \rightarrow I = ca. 300\text{ }^\circ\text{C}$; ^1H NMR (CDCl_3): δ 7.8-7.3 (m, 8H, CH_{Ar}), 4.20 (m, 16H, $-\text{OCH}_2-$), 2.2 (m, 16H, $-\text{OCH}_2\text{CH}_2-$), 1.8 (m, 16H, $-\text{OCH}_2\text{CH}_2\text{CH}_2-$), 1.3-1.2 (m, 128H, $-\text{CH}_2-$), 0.9 (m, 24H, $-\text{CH}_3$); MALDI-TOF MS (dithranol): m/z 2043-2049 (isotopic pattern) $[\text{M}]^+$; UV-vis (CHCl_3) λ_{max} ($\log \epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 672 (5.14), 605 (4.30), 311 (4.76); elemental analysis for $\text{C}_{128}\text{H}_{208}\text{N}_8\text{O}_8\text{Ni}$ (FW = 2045.8): Calcd: C 75.15%, H 10.25%, N 5.48%. Found: C 75.01%, H 9.87%, N 5.91%.

2-(3-Hydroxy-3-methyl-1-butynyl)-9,10,16,17,23,24-hexakis(dodecyloxy)phthalocyaninatonicel(II) (3)



Compound 4,5-didodecyloxyphthalonitrile¹ (712 mg, 1.43 mmol) and 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile² (100 mg, 0.48 mmol) was refluxed in dimethylaminoethanol (DMAE) (3 mL) under argon for 16 hrs in the presence of NiBr₂ (132 mg, 0.6 mmol). After this time the solution was allowed to reach room temperature and a mixture of MeOH/H₂O (1:1) was added to it. The solution was then filtered and the precipitate dissolved in CH₂Cl₂. The solution was then reduced to dryness to obtain a product that was subjected to a column chromatography on silica gel (CHCl₃) to afford the unsymmetrical Ni(II)Pc **3** (174 mg, 20% yield[§]) and the symmetrical Ni(II)Pc **2** (263 mg, 36% yield[¶]), both as blue products.

¹H NMR (CDCl₃): δ 7.5-7.2 (m, 9H, CH_{Ar}), 4.4 (s, 1H, -OH), 4.1-4.0 (t, 12H, -OCH₂-), 2.2 (m, 12H, -OCH₂CH₂), 1.9 (m, 12H, -OCH₂CH₂CH₂-), 1.6 (s, 18H, -CH₃), 1.3-1.2 (m, 84H, -CH₂-), 0.9 ppm (m, 18H, -CH₂-); MALDI-TOF MS (dithranol): *m/z* 1758-1762 (isotopic pattern) [M]⁺; IR (KBr): ν (cm⁻¹) 3445, 2923, 2872, 1283, 1075; UV-vis (CHCl₃) λ_{max} (log ε/dm³ mol⁻¹ cm⁻¹): 297 (4.88), 610 (4.32), 677 (4.90); elemental analysis for C₁₀₉H₁₆₆N₈O₇Ni (FW = 1759.2): C 74.42%, H 9.51%, N 6.37%. Found: C 74.01%, H 9.42%, N 6.33%.

1) 4,5-Didodecyloxyphthalonitrile was prepared following the same procedure used by I. Hisato, E. Katashi, O. Takahisa, N. Tumotu, Eur. Pat. Appl. EP. 373,643. (QC07F7/00), 20 Jun. 1990, 15 Dec. 1988, Chem. Abs. 114:P1333092a, for the preparation of 4,5-dibutoxyphthalonitrile.

2) E. M. Maya, P. Haisch, P. Vázquez, T. Torres, *Tetrahedron*, 1998, **54**, 4397.

§ calculated on the added 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile.

¶ calculated on the added 4,5-didodecyloxyphthalonitrile.

Table S1 Optical, thermal and thermodynamic data for Ni(II)Pc **1** and **2**.

Compound	Transition ^a	Temperature (°C) ^b	ΔH (KJ mol ⁻¹) ^b
Ni(II)Pc 1	<i>K</i> → <i>Col_h</i>	-	-
	<i>Col_h</i> → <i>I</i>	70	13.0
Ni(II)Pc 2	<i>K</i> → <i>Col_h</i>	84	77.2
	<i>Col_h</i> → <i>I</i>	<i>ca.</i> 300 ^c	-

^aDetermined by polarizing optical microscopy and X-ray diffraction. *K* = crystalline phase; *Col_h* = hexagonal columnar mesophase; *I* = isotropic liquid. ^bDetermined by DSC (first heating scan).

^cDetermined by polarizing optical microscopy.

Table S2 X-ray diffraction (XRD) data for the *Col_h* mesophase of compounds **1** and **2**. The columns report the temperature of the experiment, the proposed indexation, the observed and calculated spacing and the hexagonal lattice constant for the Ni(II)Pc **1** and **2**.

Compound	Temperature (°C)	<i>h k</i>	<i>d_{obs}</i> (Å)	<i>d_{calc}</i> (Å)	Lattice constant (Å)
Ni(II)Pc 1	25	1 0	44.2	44.2	<i>a</i> = 51.0
		1 1	25.9	25.5	
		2 0	21.8	22.1	
		3 0	14.2	14.7	
		3 1	12.2	12.25	
			4.5 (diffuse)		
			3.4		
Ni(II)Pc 2	100	1 0	31.6	31.6	<i>a</i> = 36.5
		1 1	18.4	18.25	
		2 0	15.7	15.8	
		2 1	11.9	11.95	
			4.5 (diffuse)		
			3.4		